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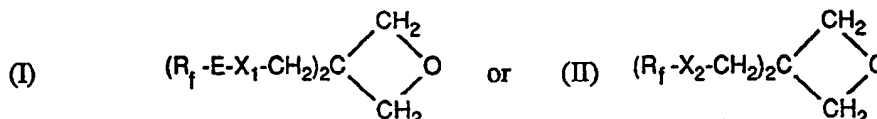
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(54) Heteroatom containing 3,3-bis perfluoroalkyl oxetanes and polyethers therefrom.

(57) Heteroatom containing perfluoroalkyl terminated oxetanes of the formula



are prepared from 3,3-dihalogenated oxetanes and thiols of the formula R_f-E-SH , amines of the formula $R_f-E-NH-R$, alcohols of the formula R_f-E-OH or perfluoro-amides, wherein R_f is a straight chain perfluoroalkyl of 1 to 18 carbon atoms.

The reaction products of these fluorinated oxetanes with nucleophiles are disclosed, as are certain functional derivatives. These products may serve as intermediates or have utility in their own right. Fluorinated polyethers derived therefrom are disclosed and include random or block compositions containing the residue from at least one R_f oxetane, containing two perfluoroalkyl hetero groups.e (ücontaining two perfluoroalkyl hetero groups.

These polyethers provide improved thermal stability and useful low surface energy oil and water repellent coatings for textiles, glass, paper, leather and other materials.

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HETEROATOM CONTAINING 3,3-BIS PERFLUOROALKYL OXETANES AND POLYETHERS THEREFROM

BACKGROUND OF THE INVENTION

This invention relates to hetero group containing perfluoroalkyl terminated oxetanes, their reaction products with nucleophiles, related halogenated derivatives, and derived polyethers. Their primary use is to impart oil and water repellency to textiles, glass, paper, leather, and other compositions.

Oxetanes connected by sulfur atoms to bis-perfluoroalkyl substituents have not been reported. Oxetanes connected by oxygen atoms to branched perfluoroalkyl groups or to fluoroalkyl groups with terminal hydrogen atoms have been described by C. Krespan in J. Org. Chem. 43, 4 (1978), Ger. Offen. 2,109,966 and 2,116,105, and by Vakhlamova, L. in C.A. 89 : 110440p and 85 : 62609w.

However, fluoroalkyl compounds which are terminally branched or contain α -hydrogen atoms do not exhibit efficient oil repellency. Perfluoroalkyl compounds which are connected directly via hetero-atoms without alkylene spacers are not sufficiently flexible as pendant groups. Perfluoroalkylmethylene-hetero groups, other than trifluoroethylene, are expensive to prepare. Consequently, such fluoroalkyl oxetanes are not practical intermediates from which to obtain useful products. Additionally, other perfluoroalkyl compounds containing heteroaromatic connecting groups or mono-fluoroalkyl oxetanes containing oxygen have been reported e.g. J. Org. Chem. 45, 3930 (1980). These compounds are not useful for purposes of this invention.

The subject perfluoroalkyl oxetanes are readily isolated in high yield and purity. Since the subject oxetanes are connected to the linear, pendant perfluoroalkyl chains by flexible hetero groups, more mobile perfluoroalkyl functions are provided, which exhibit optimal oil repellency.

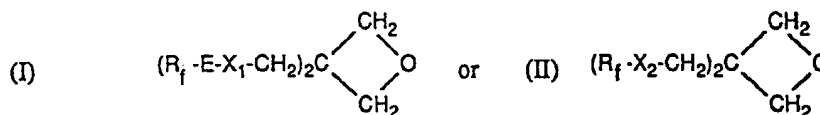
Bis-perfluoroalkyl oxetanes, polymeric derivatives thereof, and their reaction products with nucleophiles are useful because they possess a low free surface energy which provides oil and water repellency to a wide variety of substrates. Oxetanes containing a single R_f -function, multiple R_f -functions with terminal hydrogen atoms, or branched perfluoroalkyl groups are known, but do not provide these properties to the same extent. The subject oxetanes may be prepared in high yield and purity in contrast to prior art materials.

DETAILED DISCLOSURE

This invention relates to 3,3-bis-perfluoroalkyl substituted R_f -oxetanes, their derived polyethers, a heteroatom containing R_f -neopentyl compounds and the methods of making these compounds.

Another aspect of this invention relates to a substrate containing 0.1 to 10% by weight of a fluorine-containing polyether composition, at least part of said fluorine being provided by one or more units derived from the heteroatom containing R_f -neopentyl oxetane, to become oil and water repellent.

The novel heteroatom containing R_f -neopentyl oxetanes have the general formulae



wherein R_f is a straight chain perfluoroalkyl of 1 to 18 carbon atoms, E is branched or straight chain alkylene of 2 to 10 carbon atoms, or said alkylene interrupted by one to three groups selected from the group consisting of $-NR-$, $-O-$, $-S-$, $-SO_2-$, $-COO-$, $-OOC-$, $-CONR-$, $-NRCO-$, $-SO_2NR-$, and $-NRSO_2-$, or terminated at the R_f end with $-CONR-$ or $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom, or R_f-E is trifluoroethyl, X_1 is $-S-$, $-O-$, $-SO_2-$, or $-NR-$, X_2 is $-CONR-$, $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom, or X_1 and X_2 are a direct bond and where R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms.

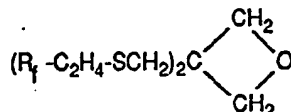
Further, the 3,3-substituents need not be identical, though identical groups are preferred.

It is understood that the R_f group usually represents a mixture of linear perfluoroalkyl moieties. When the R_f group is identified as having a certain number of carbon atoms, the said R_f group also usually concomitantly contains a small fraction of perfluoroalkyl groups with a lower number of carbon atoms and a small fraction of perfluoroalkyl groups with a higher number of carbon atoms.

Preferably the instant compounds of formula I are those where R_f is a straight chain perfluoroalkyl of 2 to 12 carbon atoms, E is alkylene of 2 to 6 carbon atoms,

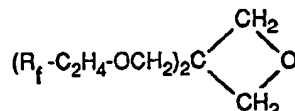
—CONHCH₂CH₂—, —CH₂CH₂N(CH₃)CH₂CH₂—, —CH₂CH₂SO₂NHCH₂CH₂—, —CH₂CH₂OCH₂CH₂—, or —SO₂NHCH₂CH₂—, and X1 is —S—, —SO₂— or —O—. A preferred embodiment is where R_f is a mixture of C₄F₉, C₆F₁₃, C₈F₁₇ and C₁₀F₂₁.

Most preferred are compounds of formula



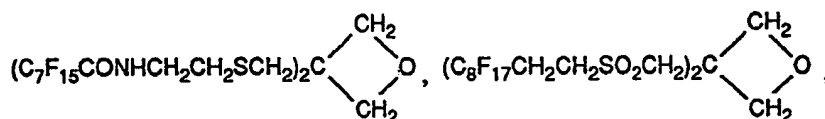
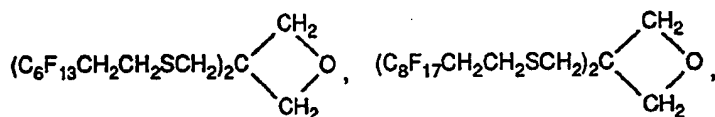
wherein R_f is perfluoroalkyl of 6 to 12 carbon atoms.

Another group of most preferred compounds is of formula

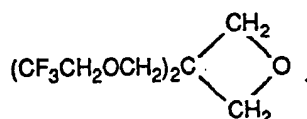


wherein R_f is perfluoroalkyl of 6 to 12 carbon atoms.

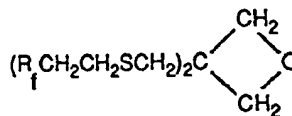
Other preferred compounds are of the formulae



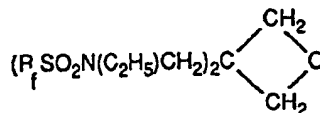
or



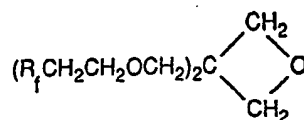
Another group of preferred compounds is of formula



wherein R_f is a mixture of C₄F₉, C₆F₁₃, C₈F₁₇ and C₁₀F₂₁, of formula

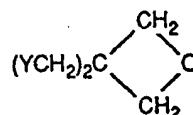


wherein R_f is a mixture of C₄F₉, C₆F₁₃, C₈F₁₇ and C₁₀F₂₁, or of formula



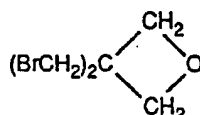
wherein R_f is a mixture of C_4F_9 , C_6F_{13} , C_8F_{17} and $\text{C}_{10}\text{F}_{21}$.

The synthesis of R_f -oxetanes proceeds by the nucleophilic substitution of a perfluoroalkyl substituted thiol, amine, alcohol or sulfonamide for halide. The novel R_f -oxetanes can be obtained directly by the reaction of a perfluoroalkyl thiol of formula $R_f\text{-E-SH}$, perfluoroalkyl amine of formula $R_f\text{-E-N(R)}_2$, perfluoroalkanol of formula $R_f\text{-E-OH}$, or a perfluoroalkylsulfonamide of formula $R_f\text{-SO}_2\text{NHR}$ with a bis-haloalkyl oxetane of formula



wherein R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms and Y is Cl , Br , or I .

In one preferred embodiment, the starting material is bis-bromomethyl oxetane and has the formula



This intermediate is commercially available in high purity. Dichloro and diiodo neopentyl oxetanes have also been reported.

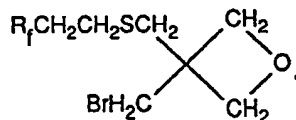
The reaction is preferably conducted in an aqueous system using phase transfer catalysis for the thiolate and amide. An alternate process, in anhydrous media, is best for the alcohol and involves the combination of:

- a. an aprotic solvent, such as N -methylpyrrolidone, N,N -dimethylformamide, dimethyl sulfoxide, or the like, or ketones, such as acetone, methyl alkyl ketones, or dialkyl ketones;
- b. moderate reaction temperature, in the order of 50 to about 120°C ; and
- c. a stoichiometric quantity of an anhydrous alkaline earth carbonate, preferably potassium carbonate, in the ratio of 1 mole of carbonate per mole of halide to be displaced.

With certain amines, tertiary amine catalysis is useful, as exemplified by triethylamine, tributylamine, dimethylaminopyridine, or piperidine. With alcohols or sulfonamides, Crown ether catalysis is useful as exemplified by 12-Crown-4, 15-Crown-5, and 18-Crown-6.

The reaction temperature and choice of solvent are mutually dependent. A reaction temperature in the range of 50 - 140°C is one wherein the formation of undesirable by-products is minimized and the reaction products are stable. Conditions are adjusted in order to achieve a reasonable rate of reaction at the chosen temperature.

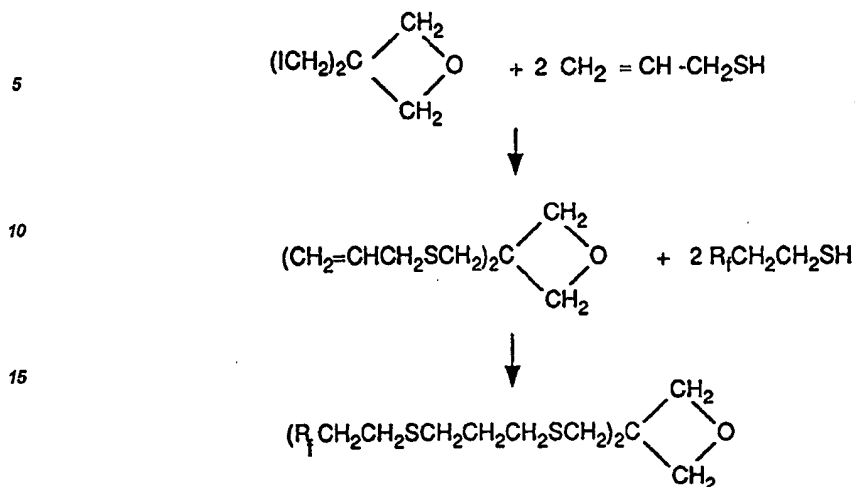
In the synthesis of the R_f -oxetanes, by-products may be present. When the starting thiol is $R_f\text{CH}_2\text{CH}_2\text{SH}$ and bis-bromomethyl oxetane is used, the by-products include



Such an intermediate is consistent with the general reaction conditions. It should be noted that the ready oxidation of thiols to disulfides requires that the chemistry be conducted in an inert atmosphere.

The subject oxetanes can also be obtained by first reacting the bromo-oxetane intermediates with a functional thiol or amine, i.e. $\text{HSCH}_2\text{CH}=\text{CH}_2$, HSCH_2COOH or $\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2$. The resultant sulfide or amide can then be reacted with the R_f -containing moiety by a suitable chemistry which does not involve the pendant oxetane. The reactant may be R_f , $R_f\text{CH}_2\text{CH}_2$, $R_f\text{CH}_2\text{CH}_2\text{OH}$ or a similar monofunctional R_f -reactant. If iodine atoms are introduced they may be removed by reduction, dehydrohalogenation, or coupling.

For example



The subject sulfido-oxetanes can be readily oxidized to the corresponding bis-sulfone oxetanes by peracetic acid (H_2O_2 /acetic acid) or by other conventional oxidants. With peracetic acid, temperatures of 30-100°C are appropriate depending on the amount of excess oxidizing agent to ensure that the intermediate sulfoxides are completely oxidized.

Perfluoroalkyl thiols useful herein are well documented in the prior art. For example, thiols of the formula $\text{R}_f\text{-E-SH}$ have been described in a number of U.S. Patent Nos. including 3,655,732 and 4,584,143.

Thus, U.S. Patent No. 3,655,732 discloses mercaptans of formula $\text{R}_f\text{-E-SH}$ wherein E is alkylene of 1 to 16 carbon atoms and R_f is perfluoroalkyl, and teaches that halides of formula $\text{R}_f\text{-E-Halide}$ are well known; reaction of $\text{R}_f\text{-I}$ with ethylene under free-radical conditions gives $\text{R}_f(\text{CH}_2\text{CH}_2)\text{I}$ while reaction of $\text{R}_f\text{CH}_2\text{I}$ with ethylene gives $\text{R}_f\text{CH}_2(\text{CH}_2\text{CH}_2)\text{I}$ as is further taught in U.S. Patent Nos., 3,088,849, 2,965,659 and 2,972,638.

U.S. Patent No. 3,655,732 further discloses compounds of formula $\text{R}_f\text{-R}'\text{-Y-R}''\text{-SH}$ wherein R' and R'' are alkylene of 1 to 16 carbon atoms, with the sum of the carbon atoms of R' and R'' being no greater than 25; R_f is perfluoroalkyl of 4 through 14 carbon atoms and Y is -S- or -NR^m- where R^m is hydrogen or alkyl of 1 through 4 carbon atoms.

U.S. Pat. No. 3,544,663 teaches that the mercaptan $\text{R}_f\text{CH}_2\text{CH}_2\text{SH}$ where R_f is perfluoroalkyl of 5 to 13 carbon atoms, can be prepared by reacting the perfluoroalkyl alkylene iodide with thiourea or by adding H_2S to a perfluoroalkyl substituted ethylene ($\text{R}_f\text{-CH}=\text{CH}_2$), which in turn can be prepared by dehydrohalogenation of the $\text{R}_f\text{-CH}_2\text{CH}_2\text{-halide}$.

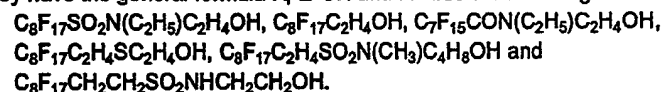
The reaction of the iodide $\text{R}_f\text{-E-I}$ with thiourea followed by hydrolysis to obtain the mercaptan $\text{R}_f\text{-E-SH}$ is the preferred synthetic route. The reaction is applicable to both linear and branched chain iodides.

Particularly preferred herein are the thiols of formula $\text{R}_f\text{CH}_2\text{CH}_2\text{SH}$ wherein R_f is perfluoroalkyl of 6 to 12 carbon atoms. These R_f -thiols can be prepared from $\text{R}_f\text{CH}_2\text{CH}_2\text{I}$ and thiourea in a very high yield.

Perfluoroalkylamines useful herein are well documented in the prior art. For example, $\text{C}_8\text{F}_{13}\text{CH}_2\text{CH}_2\text{NH}_2$ has been described in Japan Kokai 77/118,406. $\text{R}_f\text{CH}_2\text{NH}_2$ wherein R_f is CF_3 through $\text{CF}_3(\text{CF}_2)_{11}$ are described in British Patent No. 717,232 (1954).

Further $\text{R}_f(\text{SO}_2\text{NRCH}_2\text{NR}(\text{CH}_2)_3\text{NH}_2)$ and $\text{R}_f\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_2\text{N}(\text{R})_2$ are described in G.B. 1,106,641 and U.S. 3,838,165 respectively; $\text{R}_f\text{CONHCH}_2\text{NH}_2$ in Jap. Kokai 52/14767.

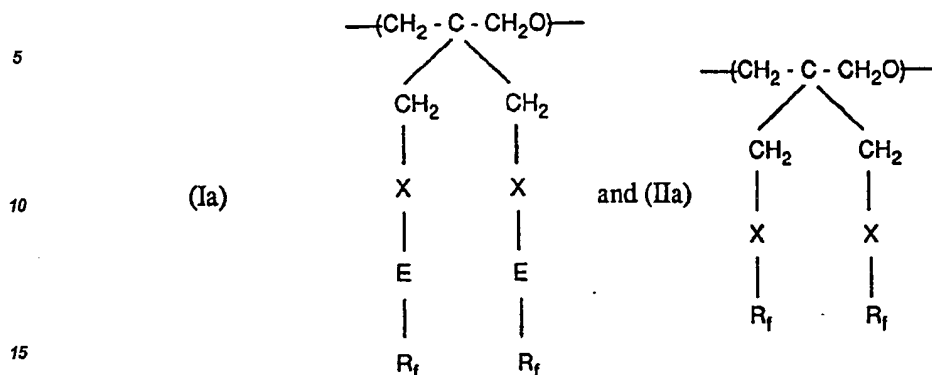
Perfluoroalkanols useful herein are well documented in the prior art, and many are commercially available. They have the general formula $\text{R}_f\text{-E-OH}$ and include the following:



Perfluoroalkylsulfonamides useful herein are well documented in the prior art such as in U.S. 2,915,554 and include compounds of the general structure $\text{R}_f\text{-SO}_2\text{NHR}$, such as $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{OH}$, $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_3)\text{H}$, $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{i-C}_3\text{H}_7)\text{H}$, $\text{C}_{10}\text{F}_{21}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{H}$ and $\text{C}_{10}\text{F}_{21}\text{SO}_2\text{NH}_2$.

The oxetanes can be used directly or indirectly by reaction with nucleophiles to make a variety of products. Such nucleophiles as halide ions, thiourea, alcohols and thiols can be used as described in Heterocyclic Compounds by Weissberger, Vol. 19 (II), under Oxetanes by S. Searles, Jr.

The instant invention also relates to novel linear polyethers which are derived from the aforementioned oxetanes having recurring structural units of the formulae



wherein R_f is a straight chain perfluoroalkyl of 1 to 18 carbon atoms, E is branched or straight chain alkylene of 2 to 10 carbon atoms, or said alkylene interrupted by one to three groups selected from the group consisting of ---NR--- , ---O--- , ---S--- , $\text{---SO}_2\text{---}$, ---COO--- , ---OOC--- , ---CONR--- , ---NRCO--- , $\text{---SO}_2\text{NR---}$, and $\text{---NRSO}_2\text{---}$, or terminated at the R_f end with ---CONR--- or $\text{---SO}_2\text{NR---}$, where R_f is attached to the carbon or sulfur atom, or $R_f\text{---E}$ is trifluoroethyl, or for formula Ia, X is ---S--- , ---O--- , $\text{---SO}_2\text{---}$, or ---NR--- , and for formula IIa, X is ---CONR--- , $\text{---SO}_2\text{NR---}$, or a direct bond where R_f is attached to the carbon or sulfur atom, and where R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms.

In one embodiment, the polyethers are homopolymers, in another they are block polymers and contain 1-90% of a fluorochemical block connected to 99-10% by weight of a non-fluorochemical block.

Polyethers derived from non-fluorinated oxetanes are well known and are also described by Searles in the previous citation. The polymer of 3,3-bis(chloromethyl) oxetane was known commercially as "Penton" and has good electrical molding, dimensional stability and solubility properties. It is no longer manufactured.

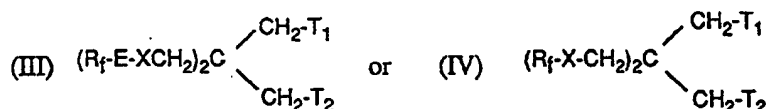
The derived polyethers of the present invention are generally prepared from the corresponding oxetane monomer by cationic polymerization, most typically with a powerful electrophilic agent such as boron trifluoride or its etherate. Polymerization occurs rapidly and exothermically and is generally conducted in solution. A co-catalyst of water appears necessary and high molecular weight polymers can be obtained.

Numerous 3,3-disubstituted oxetanes have been reported, including several highly branched perfluoroalkyl derivatives, and several have been polymerized.

Polyethers derived from the instant linear 3,3-bis-perfluoroalkyl oxetanes can also be copolymerized with tetrahydrofuran and block copolymers prepared by the method taught by S.V. Conjeevaram, et. al. in J. Polymer Sci., 23,429-444 (1985).

The polyethers of the present invention have extremely low free surface energies and therefore, possess oil and water repellent properties, as well as mold release and other properties associated with low free surface energy. It should be noted that the compounds of this invention are characterized by the presence of two perfluoroalkylhetero groups, in close proximity, a characteristic which provides improved oil and water repellent

The instant invention also relates to novel heteroatom containing R_f -neopentyl compounds of the formulae



wherein R_f is a straight chain perfluoroalkyl of 1 to 18 carbon atoms, E is branched or straight chain alkylene of 2 to 10 carbon atoms, or said alkylene interrupted by one to three groups selected from the group consisting of ---NR--- , ---O--- , ---S--- , $\text{---SO}_2\text{---}$, ---COO--- , ---OOC--- , ---CONR--- , ---NRCO--- , $\text{---SO}_2\text{NR---}$, and $\text{---NRSO}_2\text{---}$, or terminated at the R_f end with ---CONR--- or $\text{---SO}_2\text{NR---}$, where R_f is attached to the carbon or sulfur atom, $R_f\text{---E}$ is trifluoroethyl, and for formula III, X is ---S--- , ---O--- , $\text{---SO}_2\text{---}$, or ---NR--- , or for formula IV, X is ---CONR--- , $\text{---SO}_2\text{NR---}$, or a direct bond where R_f is attached to the carbon or sulfur atom, and where R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms, and T_1 and T_2 are independently chloro, bromo, or iodo, or where one of T_1 and T_2 is hydroxyl, alkanoyloxy of 2 to

18 carbon atoms, alkenoyloxy of 2 to 18 carbon atoms or benzoyloxy, and the other of T₁ and T₂ is defined above.

When one of T₁ and T₂ is alkanoyloxy, said group is for example acetoxo, propionyloxy, butyryloxy, caproyloxy, capryloyloxy, nonanoyloxy, lauroyloxy or octadecanoyloxy.

When one of T₁ and T₂ is alkenoyloxy, said group is for example acryloyloxy, methacryloyloxy or oleoyloxy.

Preferably one of T₁ and T₂ is hydroxyl and the other of T₁ and T₂ is chloro, bromo, or iodo.

In another preferred embodiment, both of T₁ and T₂ are chloro, bromo or iodo, most preferably bromo.

It is understood that the R_f group usually represents a mixture of linear perfluoroalkyl moieties. When the R_f group is identified as having a certain number of carbon atoms, the said R_f group also usually concomitantly contains a small fraction of perfluoroalkyl groups with a lower number of carbon atoms and a small fraction of perfluoroalkyl groups with a higher number of carbon atoms.

Preferably the instant compounds of formula III are those wherein R_f is perfluoroalkyl of 2 to 12 carbon atoms, E is alkylene of 2 to 6 carbon atoms, —CONHCH₂CH₂—, —CH₂CH₂N(CH₃)CH₂CH₂—, —CH₂CH₂SO₂NHCH₂CH₂—, —CH₂CH₂OCH₂CH₂—, or —SO₂NHCH₂CH₂—, and X is —S—, —SO₂— or —O—.

A preferred embodiment is where R_f is a mixture of C₄F₉, C₆F₁₃, C₈F₁₇ and C₁₀F₂₁.

Most preferred are those compounds of formula III wherein R_f is perfluoroalkyl of 6 to 12 carbon atoms, E is ethylene, and X is S.

In another group of most preferred compounds R_f is perfluoroalkyl of 6 to 12 carbon atoms, E is ethylene, and X is O.

Examples for most preferred compounds are 2,2-bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-3-iodo-1-propanol, 2,2-bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-3-chloro-1-propanol, 2,2-bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-3-bromo-1-propanol, 2,2-bis(1,1,2,2-tetrahydroperfluorooctylthiomethyl)-3-bromo-1-propanol, or 2,2-bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-1,3-dibromopropane.

Furthermore, if the compounds of the present invention contain two perfluoroalkylthio groups, these groups are connected via a neopentyl moiety which does not permit the thermal elimination of mercaptan by β-elimination. Hence, these R_f-oxetanes and their derivatives with various nucleophilic species have enhanced thermal stability. It should be noted that the reaction of oxetanes and HCl, HBr, or HI yields halohydrins.

The alcohol function of these halohydrins can be halogenated to form dihalo compounds. Other chemistries normally exhibited by alcohols can be accomplished, such as esterification, etc.

The halohydrins or dihalo derivatives can also be reacted with mercapto-acids to yield bis-perfluoroalkyl carboxylates useful as paper sizes.

Using the R_f-compounds and polyethers described herein, it is possible to manufacture molds that display excellent release properties. It is also possible to prepare polymeric compositions with enhanced thermal stability.

Treatment of a textile with a fluorine-containing composition, notably a bis-perfluoroalkyl containing polymer, provides outstanding oil and water-repellent characteristics thereto.

The invention described above is illustrated by the following examples :

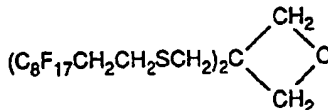
Examples 1 to 6 illustrate the preparation of the R_f-oxetanes.

Examples 7 to 11 demonstrate the wide diversity of nucleophilic reaction products and related compounds that can readily be prepared from the subject oxetanes.

Example 12 demonstrates the formation of a polyether derived from an oxetane and its excellent oil/water repellency.

Examples 13-20 show the preparation of additional R_f-substituted oxetanes.

Example 1 : 3,3-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)oxetane



3,3-Bis(bromomethyl)oxetane (15.0 g, 0.061 mol) is charged to a three neck-flask with 1,1,2,2-tetrahydroperfluorododecyl mercaptan (62.3 g, 0.13 mol). Toluene (90.0 g), distilled water (60.0 g) and sodium hydroxide (20.0 g, 50%) are added and the mixture is stirred under nitrogen. Tricaprylmethylammonium chloride, a phase transfer catalyst, (0.5 g) is then added with stirring and the reaction mixture is heated to 95°C under reflux for 2.5 hours. The toluene layer containing the product is separated hot from the lower alkaline layer by a separatory funnel and cooled to precipitate the product. The product is filtered, washed three times with cold

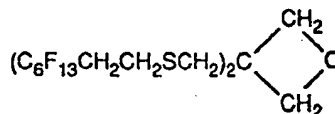
toluene and dried under vacuum to yield an off-white solid, m.p. 82-83°C, 97% purity by GLC. NMR shows proton resonances at 2.42 ppm, 4 protons, (2 x CH₂CH₂S); 2.82 ppm, 4 protons, (2 x CH₂CH₂S); 3.09 ppm, 4 protons, (2 x CH₂CH₂SCH₂); 4.56 ppm, 4 protons, (2 x CH₂OCH₂).

Analysis for C₂₅H₁₆F₃₄S₂O :

Calculated : C : 28.8% ; H : 1.5%, F : 62.0%, S : 6.2%.

Found : C : 28.6% ; H : 1.3%, F : 61.7%, S : 6.6%.

Example 2 : 3,3-Bis(1,1,2,2-tetrahydroperfluoro-octylthiomethyl)oxetane



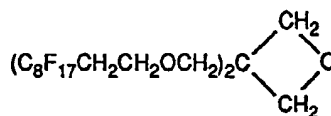
3,3-Bis(bromomethyl)oxetane (15.0 g, 0.06 mol) is charged to a three neck-flask with 1,1,2,2-tetrahydroperfluoro-octylmercaptan (51.08 g, 0.134 mol), Toluene (90.0 g), distilled water (60.0 g) and sodium hydroxide (20.0 g, 50%) are added, and the mixture is stirred under nitrogen. Tricaprylmethylammonium chloride, a phase transfer catalyst, (0.5 g) is then added with stirring and the reaction mixture is heated to 95°C under reflux for 1.5 hours. The toluene layer containing the product is separated from the lower alkaline layer and then cooled to precipitate the product. The product is filtered cold, washed three times with cold toluene and dried under vacuum to yield an off-white solid, m.p. 45.5-46°C, 99.5% purity by GLC. NMR shows proton resonances at 2.42 ppm, 4 protons, (2 x CH₂CH₂S); 2.82 ppm, 4 protons, (2 x CH₂CH₂S); 3.09 ppm, 4 protons, (2 x CH₂CH₂SCH₂); 4.45 ppm, 4 protons, (2 x CH₂OCH₂).

Analysis for C₂₁H₁₆F₂₈S₂O :

Calculated : C : 30.0% ; H : 1.9%, F : 58.6%, S : 7.6%.

Found : C : 29.8% ; H : 1.8%, F : 58.6%, S : 8.2%.

Example 3 : 3,3-Bis(1,1,2,2-tetrahydroperfluorodecyloxymethyl)oxetane



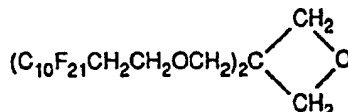
1,1,2,2-Tetrahydroperfluorooctanol (10.9 g, 0.03 mol), 3,3-(bromomethyl)oxetane (3.9 g, 0.016 mol), potassium hydroxide (1.7 g, 0.03 mol) and 15 g of diethylene glycol dimethylether are reacted in presence of approximately 1.0 g of 18 Crown-6 in a 50 ml flask with gentle stirring for 72 hours at room temperature. Analysis by gas chromatography indicates that the solution contains 36% monoadduct and 64% diadduct. 2.5 g of solids are filtered off and CG/MS identification confirms the presence of the desired 3,3-(1,1,2,2-tetrahydroperfluoro-octyloxy)oxetane and 3-(1,1,2,2-tetrahydroperfluoro-octyloxy)-3-bromo-oxetane.

Identification is made by GC/MS (E.I. Mode) after derivatization with N,O-bis-(trimethylsilyl)-trifluoroacetamide. Two major components are observed : (trimethylsilyl)-trifluoroacetamide. Two major components are observed :

Diadduct : MS : m/z 810 absent, 780 (M-CH₂O), 417 b.p., (M-C₈F₁₃CH₂CH₂O), 404 (M-C₈F₁₃CH₂CH₂OCH₂). MS (CI) 811(M+1)+

Monoadduct : MS : m/z 526 absent, 447 (M-Br), 417 b.p., (M-CH₂OBr). MS (CI) 527 (M+1)+

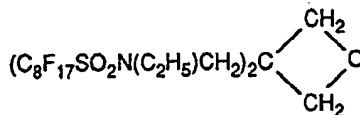
Example 4 : 3,3-Bis(1,1,2,2-tetrahydroperfluorodecyloxymethyl)oxetane



In a similar fashion to Example 3, 1,1,2,2-tetrahydroperfluorododecanol is reacted at 100°C for 2-3 hours

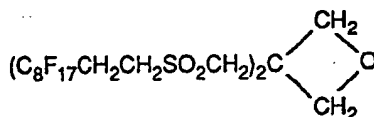
to give a mixture of monoadduct-40% and diadduct-60%.

Example 5 : 3,3-Bis(N-ethylperfluoro-octanesulfonamidomethyl)oxetane



A mixture of N-ethylperfluoro-octanesulfonamide (20.0 g, 0.047 mol), 867% potassium hydroxide (3.0 g, 0.047 mol), diethylene glycol dimethyl ether (60.0 g) and 18-Crown-6-ether (0.1 g) is heated under nitrogen at 100-105°C for 30 minutes. The 3,3-bis-(bromomethyl)-oxetane (5.7 g, 0.0236 mol), is then added, and the entire reaction mass is heated at 100°C for 13 hours. The salts are removed by filtration, and the solvent is removed at 80°C under vacuum. NMR shows the presence of the expected product.

Example 6 : 3,3-Bis(1,1,2,2-tetrahydroperfluorodecyloxymethyl)-oxetane



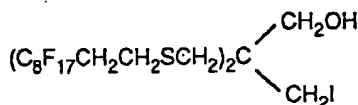
3,3-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl) (15.0 g, 0.014 mol) is dissolved in glacial acetic acid (44.27 g, 0.737 mol) and warmed to 40°C. Hydrogen peroxide (4.0 g, 30%) is added, and the mixture is stirred for 1 hour. The reaction mixture is then heated to 100°C, and additional hydrogen peroxide (11.0 g, 30%) is added. The mixture is stirred for 2.5 hours under reflux. The product, a white precipitate, is filtered, washed with ethanol and dried under vacuum, (13.85 g, 90% of theory) 93% purity by GLC. The product is recrystallized from isopropyl acetate two times and dried under vacuum to yield a white solid (8.59 g, 56% of theory), m.p. 162-4°C, 98% purity by GLC. NMR shows proton resonances at 2.90 ppm, complex, 4 protons (2 x C₈F₁₇CH₂); 3.65 ppm triplet, 4 protons, (2 x C₈F₁₇CH₂CH₂); 4.25 ppm, singlet, 4 protons, (2 x CH₂SO₂CH₂); 4.80 ppm, singlet, 4 protons, (oxetane ring).

Analysis for C₂₅H₁₆F₃₄O₅S₂:

Calculated : C : 27.1% ; H : 1.5% , F : 58.4% , S : 5.8%.

Found : C : 26.8% ; H : 1.4% , F : 58.4% , S : 5.5%.

Example 7 : 2,2-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-3-iodo-1-propanol



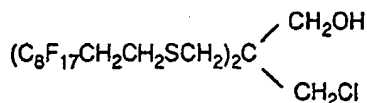
3,3-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)oxetane (2.0 g, 0.010 mol) is dissolved in tert-butyl alcohol (4.0 g, 0.054 mol). Hydriodic acid (1.0 g, 57%, 0.0045 mol) is added to the mixture, which is then heated to 60°C for 10 minutes. The product is precipitated from H₂O and then vacuum filtered. The product (1.65 g, 71% of theory) is a yellow solid, 92% purity by GLC. For analytical purposes, the crude product is crystallized from heptane, which yields a white solid (1.30 g, 56% of theory), m.p. 58-60°C, 98% purity by GLC. NMR shows proton resonances at 2.43 ppm, complex, 4 protons, (2 x C₈F₁₇CH₂); 2.72 ppm, singlet, 4 protons, (2 x SCH₂); 2.85 ppm, triplet, 4 protons, (2 x CH₂X₂S); 3.55 ppm, singlet, 2 protons, (CH₂I); 3.66 ppm, singlet, 2 protons, (CH₂OH). OH is not observed.

Analysis for C₂₅H₁₇F₃₄IOS₂:

Calculated : C : 25.7% ; H : 1.5% , F : 55.2%.

Found : C : 25.4% ; H : 1.4% , F : 54.8%.

Example 8 : 2,2-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-3-chloro-1-propanol



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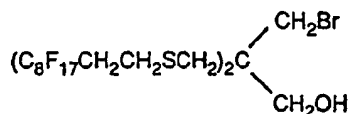
3,3-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)oxetane (1.0 g, 0.001 mol) is dissolved in tert-butyl alcohol (2.0 g, 0.054 mol). Hydrochloric acid (1.2 g, 37.7%, 0.011 mol) is added to the mixture, which is then heated to 60°C for 10 minutes. The product is precipitated from H₂O (15 g), vacuum filtered and dried in a desiccator over drierite. This procedure yields an off-white solid (0.40 g, 37% of theory), m.p. 60-1°C, 96% purity by GLC. NMR shows proton resonances at 2.4 ppm, complex, 4 protons, (2 x C₈F₁₇CH₂); 2.7 ppm, singlet, 4 protons, (2 x CH₂S); 2.85 ppm, triplet, 4 protons, (2 x SCH₂); 3.65 ppm, singlet, 4 protons, (CH₂Cl and CH₂OH). OH is not observed.

Analysis for C₂₅H₁₇F₃₄OS₂:
 Calculated: C: 27.8%; H: 1.6%, F: 59.9%.
 Found: C: 27.6%; H: 1.3%, F: 59.5%.

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Example 9: 2,2-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-3-bromo-1-propanol

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2,2-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)oxetane (7.0 g, 0.0067 mol) is charged to a three-neck flask with hydrobromic acid (48%, 2.5 g, 0.015 mol) and toluene (20.0 g). The reaction is heated at 100°C under nitrogen with stirring for 2 hours. The water/toluene azeotrope is then removed to 110°C. The toluene concentrate is then cooled and the product precipitates. The product is filtered, washed three times with cold toluene and dried under vacuum to yield a white solid, m.p. 63-64°C, 98% purity by GLC. NMR shows proton resonances at 1.70 ppm, 1 protons, (-OH); 2.25-2.60 ppm, 4 protons, (2 x R₁CH₂); 2.7-2.9 ppm, 8 protons, (2 x CH₂-S-CH₂); 3.53 ppm, 2 protons, (CH₂Br); 3.67 ppm, 2 protons, (CH₂OH).

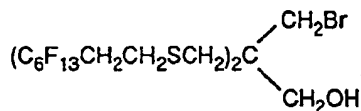
30

Analysis for C₂₅H₁₇F₃₄BrOS₂:
 Calculated: C: 26.7%; H: 1.5%, Br: 7.1%, F: 57.5%, S: 5.7%.
 Found: C: 26.4%; H: 1.4%, Br: 7.3%, F: 55.9%, S: 6.1%.

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Example 10: 2,2-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-3-bromo-1-propanol

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3,3-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)oxetane (7.0 g, 0.0083 mol) is charged to a three-neck flask with hydrobromic acid (48%, 3.1 g, 0.018 mol) and toluene (20.0 g). The reaction is heated at 100°C under nitrogen with stirring for 4 hours. The water/toluene azeotrope is then removed at 110°C. The solvent is then removed under vacuum to yield a thick brown liquid which is 99% pure by GLC. NMR shows proton resonances at 1.80 ppm, 1 protons, (-OH); 2.2-2.6 ppm, 4 protons, (2 x R₁CH₂); 2.7-2.9 ppm, 8 protons, (2 x CH₂-SCH₂); 3.53 ppm, 2 protons, (CH₂Br); 3.65 ppm, 2 protons, (CH₂OH).

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Analysis for C₂₁H₁₇OS₂F₂₆Br:
 Calculated: C: 27.3%; H: 1.9%, Br: 8.7%, F: 53.5%, S: 7.0%.
 Found: C: 27.1%; H: 1.7%, Br: 9.1%, F: 51.5%, S: 7.1%.

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Example 11: 2,2-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)1,3-dibromopropane



2,2-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-3-bromopropanol (10.0 g, 9 mmol) is charged to a

three necked flask with phosphorous tribromide (4.3 g, 16 mmol). The reaction mixture is heated at 100°C under nitrogen for 2 hours to give the desired product which is recrystallized from toluene.

Identification is made by GC/MS (E.I. mode).

MS : m/z 1184 (m+) 1165 (m-f), 739 (b.p.), 493.

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Example 12 : Poly-[2,2-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)trimethylene ether]

3,3-Bis(1,1,2,2-tetrahydroperfluorodecylthiomethyl)oxetane (10.0 g, 0.0096 mol) is dissolved in trifluorotrichloroethane and boron trifluoride etherate (2.0 ml) is added as catalyst. The reaction mixture is stirred at room temperature for 0.5 hr. The product, a white precipitate, is then vacuum filtered, washed two times with trifluorotrichloroethane and dried under high vacuum, yielding a white solid (8.44 g). Several analyses confirm the presence of the desired polymer.

Analysis for $(C_{25}H_{18}F_{34}S_2O)_n$:

Calculated : C : 28.8% ; H : 1.5% ; S : 6.1%.

Found : C : 26.6% ; H : 1.5% ; S : 6.0%.

The 1H NMR spectra obtained by silylation experiments indicates a repeat unit n of 9-10.

DSC scans of the polymer were run at 10°C/min. to 350°C, 100 ml N_2 /min. in open aluminum pans with a DuPont 990 Thermal Analyzer and a DSC cell base. The scans indicate an endothermic melting transition (T_x (extrapolated onset temperature) = 116°C, $T_{peak} = 121^\circ C$), irreversible decomposition transitions ($T_{peak} = 140^\circ C$ and $164^\circ C$) and a major irreversible decomposition transition ($T_{peak} = 243^\circ C$).

TGA scans were run at 10°C/min. to 550°C, 100 ml N_2 /min. using a DuPont 951 TGA module. The scans show a 22% weight loss from 150-305°C and a second weight loss of 73% from 305-450°C. A 1% residue remains at 450°C. (A 4% weight loss before $T = 150^\circ C$ is attributed to solvent loss).

Using the Zisman technique, the critical surface tension of the polymer γ_c , is found to be 9.8 dyne/cm. This indicates that the polymer is oil and water repellant.

When a solution of said polyether in hexafluoroxylene is used to treat a textile surface to deposit 0.1% by weight thereon, the textile surfaces becomes oil and water repellant.

Examples 13 to 19 : Using the methods described and by techniques similar to Examples 1-6, the following additional perfluoroalkyl substituted oxetanes are prepared.

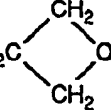
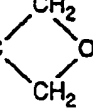
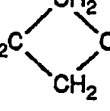
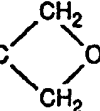
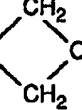
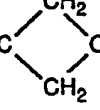
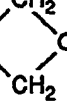
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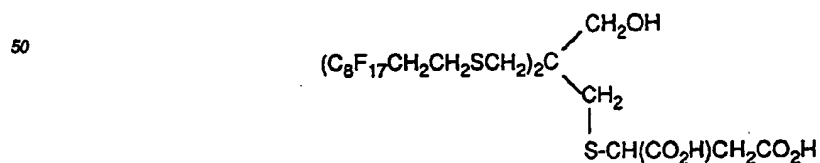
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	Ex.	Thiol	Perfluoroalkyl Terminated Neopentyl Oxetane
5	13	$\text{CF}_3\text{CF}_2\text{CH}_2\text{SH}$	$(\text{CF}_3\text{CF}_2\text{CH}_2\text{SCH}_2)_2\text{C}$ 
10	14	$\text{C}_6\text{F}_{13}(\text{CH}_2)_4\text{SH}$	$(\text{C}_6\text{F}_{13}(\text{CH}_2)_4\text{SO}_2\text{CH}_2)_2\text{C}$ 
15	15	$\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{SH}$	$(\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{SCH}_2)_2\text{C}$ 
20	16	$\text{C}_8\text{F}_{17}(\text{CH}_2)_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{SH}$	$(\text{C}_8\text{F}_{17}(\text{CH}_2)_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{SCH}_2)_2\text{C}$ 
25	17	$\text{C}_8\text{F}_{17}\text{SO}_2\text{NHCH}_2\text{CH}_2\text{OH}$	$(\text{C}_8\text{F}_{17}\text{SO}_2\text{NHCH}_2\text{CH}_2\text{OCH}_2)_2\text{C}$ 
30	18	$\text{C}_8\text{F}_{17}(\text{CH}_2)_2\text{SO}_2\text{NH}(\text{CH}_2)_2\text{SH}$	$(\text{C}_8\text{F}_{17}(\text{CH}_2)_2\text{SO}_2\text{NH}(\text{CH}_2)_2\text{SCH}_2)_2\text{C}$ 
35	19	$\text{C}_7\text{F}_{15}\text{CONHCH}_2\text{CH}_2\text{SH}$	$(\text{C}_7\text{F}_{15}\text{CONH}(\text{CH}_2)_2\text{SCH}_2)_2\text{C}$ 

Examples 20-27 : Using the methods described and by techniques similar to Examples 7-12, the following additional alcohols, dihalides, esters and polymers are prepared.

<u>Ex.</u>	<u>Product</u>
5 20	$(\text{CF}_3\text{CF}_2\text{CH}_2\text{SCH}_2)_2\text{C} \begin{array}{l} \text{CH}_2\text{OH} \\ \text{CH}_2\text{Br} \end{array}$
10 21	$(\text{C}_8\text{F}_{17}\text{SO}_2\text{NHCH}_2\text{CH}_2\text{SCH}_2)_2\text{C} \begin{array}{l} \text{CH}_2\text{OH} \\ \text{CH}_2\text{I} \end{array}$
15 22	$(\text{C}_7\text{F}_{15}\text{CONHCH}_2\text{CH}_2\text{SCH}_2)_2\text{C} \begin{array}{l} \text{CH}_2\text{Br} \\ \text{CH}_2\text{Br} \end{array}$
20 23	$(\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{SO}_2\text{NHC}_2\text{H}_4\text{SCH}_2)_2\text{C} \begin{array}{l} \text{CH}_2\text{Br} \\ \text{CH}_2\text{Cl} \end{array}$
25 24	$(\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OCH}_2)_2\text{C} \begin{array}{l} \text{CH}_2\text{OH} \\ \text{CH}_2\text{I} \end{array}$
30 25	$(\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{SCH}_2)_2\text{C} \begin{array}{l} \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH}_3 \\ \text{CH}_2\text{Br} \end{array}$
35 26	$(\text{C}_{10}\text{F}_{21}\text{CH}_2\text{CH}_2\text{SO}_2\text{CH}_2)_2\text{C} \begin{array}{l} \text{CH}_2\text{O}_2\text{C}(\text{CH}_2)_7\text{CH}_3 \\ \text{CH}_2\text{Br} \end{array}$
40 27	Poly[2,2-bis(1,1,2,2-tetrahydrotri- fluoropropylloxymethyl)trimethylene ether].

Example 28 : 2,2-Bis-(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-3-(2,3-dicarboxy-1-thiopropyl)-1-propanol



The bromohydrin of Example 9 (17.4 g, 16.6 mmol), diethyl thiosuccinate (6.5 g, 31 mmol), potassium carbonate (4.3 g, 31 mmol) and acetone (50 ml) are charged to a three-neck flask and heated at reflux overnight. Water is added and the mixture extracted three times with methyl propyl ketone. The product is purified by silica

chromatography to yield a yellow oil which is 99% pure by GLC.

The above diethyl ester (9.5 g, 7.6 mmol) is dissolved in 20 ml of diglyme and water (3 ml) in a single neck flask. Sodium hydroxide (1.5 ml) of a 50% aqueous solution) is added and the mixture allowed to stir overnight at room temperature. Water is added, and the mixture extracted with methyl propyl ketone. The aqueous layer
 5 was acidified and extracted with methyl propyl ketone. The solvent is removed under vacuum and the resultant yellow oil is precipitated into water to produce a white solid. NMR shows proton resonances at 2.5 ppm (4 x R_fCH_2); 2.6-3.0 ppm (10 x SCH_2); 3.51 ppm (2 x CH_2OH); 3.72 (1 x $SCHCO_2$).

Analysis for $C_{29}H_{22}F_{34}S_3O_5$:

Calculated: C: 29.2%; H: 1.8%; F: 54.1%; S: 8.1%.

10 Found: C: 28.9%; H: 1.7%; F: 53.9%; S: 8.2%.

Example 29: 2,2-Bis-(1,1,2,2-tetrahydroperfluorodecylthiomethyl)-1,3-(2-carboxy-1-thiaethyl) propane

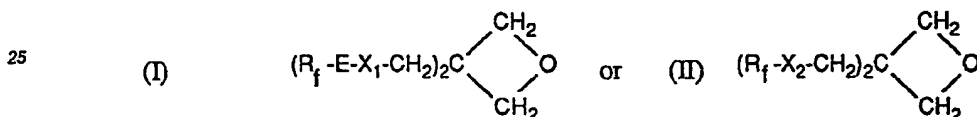
$(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2SCH_2CO_2H)_2$

15 The dibromide from Example 11 (25 g, 21 mmol), ethyl 2-mercaptoacetate (5.1 g, 41 mmol), potassium carbonate (5.8 g, 42 mmol), and acetone (70 ml) is reacted and purified as described in Example 28.

The resultant diester is saponified, acidified and precipitated into water to yield a white powder.

20 **Claims**

1. A compound of the formula

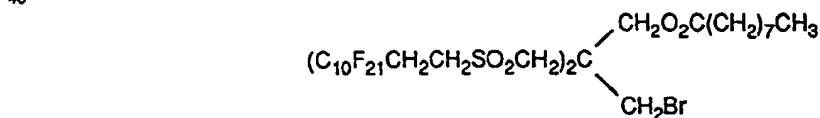


wherein R_f is a straight chain perfluoroalkyl of 1 to 18 carbon atoms, E is branched or straight chain alkylene of 2 to 10 carbon atoms, or said alkylene is interrupted by one to three groups selected from the group consisting of $-NR-$, $-O-$, $-S-$, $-SO_2-$, $-COO-$, $-OOC-$, $-CONR-$, $-NRCO-$, $-SO_2NR-$, and $-NRSO_2-$, or terminated at the R_f end with $-CONR-$ or $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom, or R_f-E is trifluoroethyl, X_1 is $-S-$, $-O-$, $-SO_2-$ or $-NR-$, X_2 is $-CONR-$, $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom, or X_1 and X_2 are a direct bond and where
 35 R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms.

2. A compound of formula I according to claim 1 where R_f is a straight chain perfluoroalkyl of 2 to 12 carbon atoms, E is alkylene of 2 to 6 carbon atoms,
 40 $-CONHCH_2CH_2-$, $-CH_2CH_2N(CH_3)CH_2CH_2-$, $-CH_2CH_2SO_2NHCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2-$, or $-SO_2NHCH_2CH_2-$, and X_1 is $-S-$, $-SO_2-$ or $-O-$.

3. A compound according to claim 1 or 2, wherein R_f is a mixture of C_4F_9 , C_6F_{13} , C_8F_{17} and $C_{10}F_{21}$.

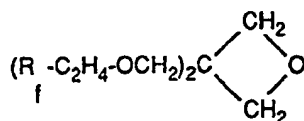
4. A compound according to one of claims 1 to 3 of formula



50 wherein R_f is perfluoroalkyl of 6 to 12 carbon atoms.

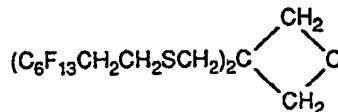
5. A compound according to one of claims 1 to 3 of formula

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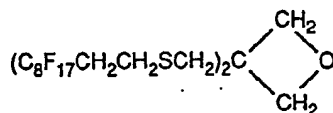


wherein R_f is perfluoroalkyl of 6 to 12 carbon atoms.

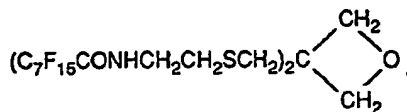
6. A compound according to one of claims 1 to 3 which is



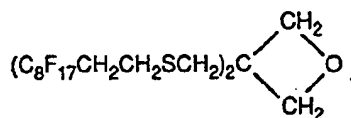
7. A compound according to one of claims 1 to 3 which is



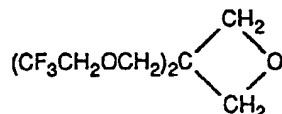
8. A compound according to one of claims 1 to 3 which is



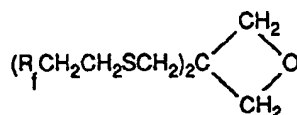
9. A compound according to one of claims 1 to 3 which is



10. A compound according to one of claims 1 to 3 which is

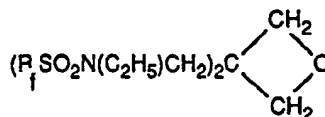


11. A compound according to one of claims 1 to 3 which is



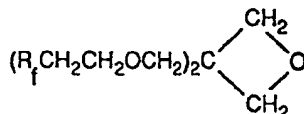
wherein R_f is a mixture of C_4F_9 , C_6F_{13} , C_8F_{17} and $C_{10}F_{21}$.

12. A compound according to one of claims 1 to 3 which is



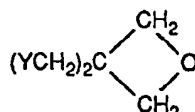
wherein R_f is a mixture of C_4F_9 , C_6F_{13} , C_8F_{17} and $C_{10}F_{21}$.

13. A compound according to claim 3 which is



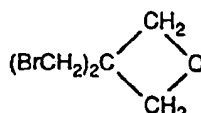
wherein R_f is a mixture of C_4F_9 , C_6F_{13} , C_8F_{17} and $C_{10}F_{21}$.

14. Process for preparation of the compounds of formulae I and II according to claim 1 by the reaction of a perfluoroalkyl thiol of formula R_f-E-SH , perfluoroalkyl amine of formula $R_f-E-N(R)_2$, perfluoroalkanol of formula R_f-E-OH , or a perfluoroalkylsulfonamide of formula R_f-SO_2NHR with a bis-haloalkyl oxetane of formula

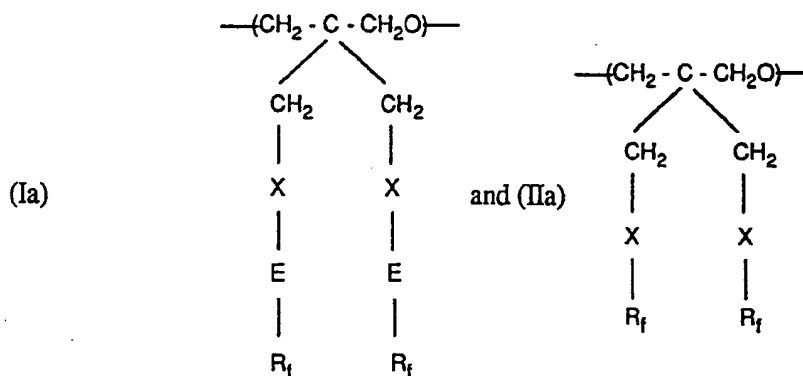


wherein R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms and Y is Cl , Br , or I .

15. Process according to claim 14, wherein the bis-haloalkyl oxetane is bis-bromomethyl oxetane of the formula



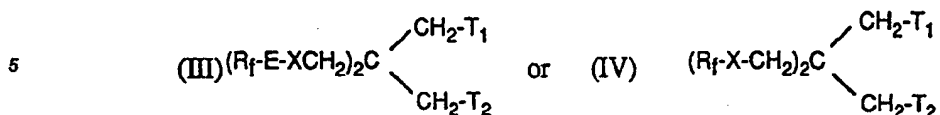
16. A linear polyether having recurring structural units of the formulae



wherein R_f is a straight chain perfluoroalkyl of 1 to 18 carbon atoms, E is branched or straight chain alkylene of 2 to 10 carbon atoms, or said alkylene is interrupted by one to three groups selected from the group consisting of $-\text{NR}-$, $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{COO}-$, $-\text{OOC}-$, $-\text{CONR}-$, $-\text{NRCO}-$, $-\text{SO}_2\text{NR}-$, and $-\text{NRSO}_2-$, or terminated at the R_f end with $-\text{CONR}-$ or $-\text{SO}_2\text{NR}-$, where R_f is attached to the carbon or sulfur atom, or R_f-E is trifluoroethyl, or for formula Ia, X is $-\text{S}-$, $-\text{O}-$, $-\text{SO}_2-$, or $-\text{NR}-$, and for formula IIa, X is $-\text{CONR}-$, $-\text{SO}_2\text{NR}-$, or a direct bond where R_f is attached to the carbon or sulfur atom, and where R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms.

17. Process for preparation of the compounds of formulae Ia or IIa of claim 16 by cationic polymerization of the corresponding oxetane monomer.

18. A heteroatom containing R_f -neopentyl compound of the formulae



10 wherein R_f is a straight chain perfluoroalkyl of 1 to 18 carbon atoms, E is branched or straight chain alkylene of 2 to 10 carbon atoms or said alkylene interrupted by one to three groups selected from the group consisting of $-NR-$, $-O-$, $-S-$, $-SO_2-$, $-COO-$, $-OOC-$, $-CONR-$, $-NRCO-$, $-SO_2NR-$, and $-NRSO_2-$, or terminated at the R_f end with $-CONR-$ or $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom, or R_f-E is trifluoroethyl, and for formula III, X is $-S-$, $-O-$, $-SO_2-$ or $-NR-$, or for formula IV, X is $-CONR-$, or $-SO_2NR-$, or a direct bond where R_f is attached to the carbon or sulfur atom, and where R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms, and T_1 and T_2 are independently chloro, bromo or iodo, or where one of T_1 and T_2 is hydroxyl, alkanoyloxy of 2 to 18 carbon atoms, alkenoyloxy of 2 to 18 carbon atoms or benzoyloxy, and the other of T_1 and T_2 is as defined above.

20 19. A compound of formula III according to claim 18 wherein R_f is perfluoroalkyl of 2 to 12 carbon atoms, E is alkylene of 2 to 6 carbon atoms, $-CONHCH_2CH_2-$, $-CH_2CH_2N(CH_3)CH_2CH_2-$, $-CH_2CH_2SO_2NHCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2-$, or $-SO_2NHCH_2CH_2-$, and X is $-S-$, $-SO_2-$ or $-O-$.

25 20. A compound according to claim 18 wherein R_f is a mixture of C_4F_9 , C_6F_{13} , C_8F_{17} and $C_{10}F_{21}$.

21. A compound of formula III according to claim 18 wherein R_f is perfluoroalkyl of 6 to 12 carbon atoms, E is ethylene and X is $-S-$.

30 22. A compound of formula III according to claim 18 wherein R_f is perfluoroalkyl of 6 to 12 carbon atoms, E is ethylene and X is $-O-$.

23. A compound according to claim 18 wherein one of T_1 and T_2 is hydroxyl, and the other of T_1 and T_2 is chloro, bromo or iodo.

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24. A compound according to claim 18 wherein both of T_1 and T_2 are chloro, bromo or iodo.

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